

Corrosion of Commercially Pure Titanium in a Sea Water Electro-Chlorination Equipment

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Corrosion mechanism of commercially pure titanium (Ti) fasteners and spacers used as parts of cathodes in sea water electro-chlorination equipment is investigated. Instrumental analysis of the corroded surfaces shows that the Ti fasteners and spacers with microstructural defects, such as micro pores, are very prone to form Ti hydride on their surfaces under the equipment operating condition, i.e., applied voltage and current. The developed brittle Ti hydride layer has many cracks in it and, therefore, is very easy to be spalled off. It is believed, with some reasonable evidences, that the internal defects are resulted from an improper powder metallurgy process of the Ti fasteners and spacers manufacturing. Use of Ti products without internal defects is recommended as the best preventive measure. Other remedial measures with some consideration of corrosion mechanism of Ti in sea water are also discussed.

Keywords : titanium, titanium hydride, micro pore, powder metallurgy, electro-chlorination

1. Introduction

Sea water electro-chlorination equipments are widely used in the cooling water systems of electrical power plants. Strong biocide, such as sodium hypochlorite (NaOCl), is produced by the sea water electrolysis,¹⁾ and used to prevent the microbiologically influenced corrosion of the cooling water system components.

Of the several commercial types of electro-chlorination equipment, most of the Korea Electric Power Corporation (KEPCO) power plants are using the so called 'plate cell' type equipment. One example of this type electro-chlorination equipment is shown in Fig. 1. The equipment is composed of several consecutive 'cell's, in which are vertically stacked plates of alternate anodes and cathodes as shown in Fig. 1(b).

Recently some spacers and fasteners (hex nuts), which are used to hold the cathodes evenly and firmly, were severely corroded as shown in Fig. 2, while there was no corrosion of spacers and fasteners at the anodes. All the materials used for the fasteners, spacers, and electrode plates for both anodes and cathodes are the same commercially pure Titanium (Ti) grade 2 (UNS R50400). Titanium is a very well known⁵⁾ corrosion resistant material for this sea water electro-chlorination environment, which is very corrosive.

Therefore, the mechanism of the corrosion failure of the normally corrosion resistant Ti is investigated and the

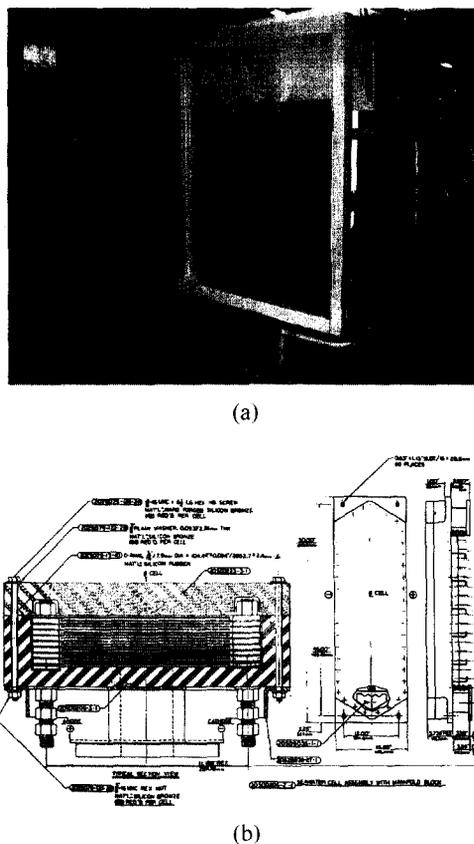


Fig. 1. A 'plate cell' type sea water electro-chlorination equipment. (a) external view, (b) schematic cross cut diagrams of a 'cell' appropriate remedial measures are also suggested based

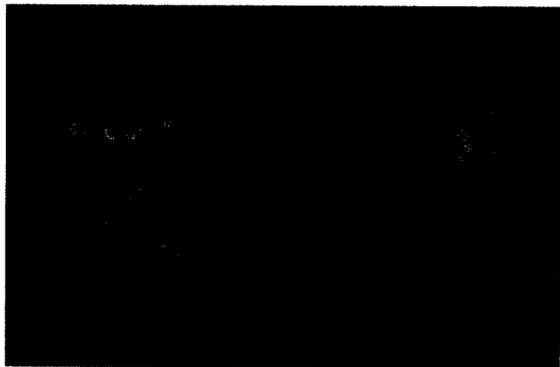


Fig. 2. An example of corroded Ti fastener (hex nut, left) and spacer (right).

on the investigation results.

2. Failure analysis

To find out the corrosion failure mechanism of the Titanium used in the sea water electro-chlorination equipment, both the corroded and the uncorroded specimens are collected from the equipment. Several mechanical and metallurgical examinations, such as surface hardness measurement, SEM (Scanning Electron Microscope) analysis with EDX (Energy Dispersive X-ray Spectroscopy), and XRD (X-Ray Diffractometer) analysis, are carried out. Each examination results are explained here in detail.

2.1 Surface hardness measurement

Surface hardness (HRB: Rockwell B scale) of the corroded and uncorroded specimens are measured according to the standard hardness measurement process.³⁾ The results are shown in Table 1. The hardnesses of the corroded specimens are much lower than that of the uncorroded specimen. This result came from the microstructural difference between the specimens, which will be explained in the next scanning electron microscope analysis section.

Table 1. Surface hardness (HRB) of the corroded and uncorroded specimens

	corroded specimen #1	Corroded specimen #2	uncorroded specimen
HRB*	68.7	73.5	95.8

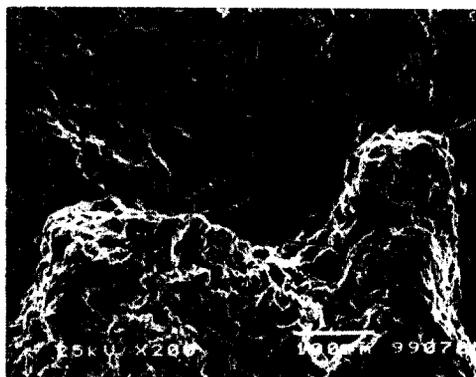
*: average of 5 measurements

2.2 SEM (scanning electron microscope) analysis

SEM images of corroded surface of a fastener specimen are shown in Fig. 3. The corroded surface, shown in Fig. 3(a), has a kind of layered structure, which is very easy



(a)



(b)

Fig. 3. SEM images of a corroded surface of a fastener specimen. (a) low magnification which shows layer type corroded surface, (b) high magnification reveals the micro pores

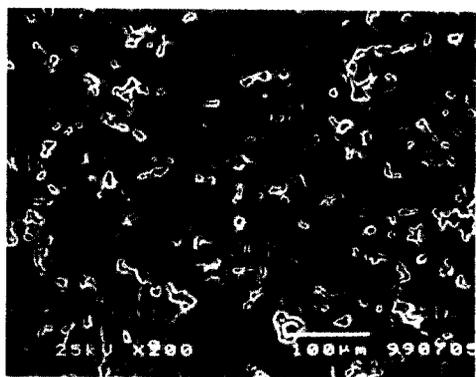


Fig. 4. SEM image of a barely corroded area surface of a fastener specimen. Micro pores exist even without corrosion.

to be spalled off by small impact such as light hitting with a pair of tweezers. A higher magnification image shows that the corroded surface has many micro pores in it as shown in Fig. 3(b). Fig. 4 shows a different surface area of the same fastener specimen where corrosion barely occurred. This area also exhibit many pores. Therefore,

it seems that the micro pores found in the fastener specimen are not the result of corrosion but the inherently existing defects of the specimen.

In order to ensure that the micro pores are pre-existing microstructural defects, a cross cut surface of the corroded fastener was examined using SEM. The SEM micrographs of this cross cut surface are shown in Fig. 5. These figures clearly reveal that there are many micro pores uniformly distributed across the whole thickness of the specimen. This means that the micro pores are inherently existing defects. Fig. 5(a) also indicates that there are many cracks developed at the near corrosion surface. The cracks are found within a narrow range of about 100 μm from the corrosion surface. Since the cracks are connecting between the micro pores, and growing mostly only in one direction, parallel to the surface, the corrosion surface looks like a layered structure as shown in Fig 3(a). The easy spalling off behavior of corroded surface also resulted from these cracks developed near the surface region.

When there are micro pores in the structure, not only the mechanical properties but also the corrosion resistance of the material are degraded. Wrought titanium products



(a)



(b)

Fig. 5. SEM images of a cross cut surface of the corroded fastener specimen.(a) near corrosion surface region, (b) inner area

usually have no such defects in it. In this corrosion failure case, therefore, considering the pore size and distribution, the Ti products are believed to be produced by the powder metallurgy techniques.

Fasteners or spacers produced by powder metallurgy technique are usually undergone a densification process,⁴⁾ such as HIP (Hot Isostatic Press), to eliminate the micro pores. But the microstructure of the corroded specimens indicates that the densification process for these specimens was omitted or improperly carried out.

One of the micro pores found at the inner area is shown in Fig. 6. EDX (Energy Dispersive X-ray Spectroscopy) analysis result of the dark spots found within the micro pore is given in Fig. 7. The EDX analysis shows calcium (Ca) is existing in the micro pores. Calcium is usually found in the powder metallurgy products, because Ca is easily segregated during the degassing process.^{4),5)} The existence of Ca within the micro pores supports that the corroded specimens are not the wrought products but the powder metallurgy products.

An examination using SEM on the uncorroded specimen cross cut surface is shown in Fig. 8. Quite contrary to the cross cut surface of the corroded specimen shown in Fig. 5, the microstructure reveals no micro pores. This means that this uncorroded specimen is not a powder metallurgy product, but a wrought product.⁶⁾ There has been no report of corrosion failure with this type of wrought Ti products so far at the KEPCO power plants.

2.3 XRD (x-ray diffractometer) analysis

The result of XRD analysis on the corroded surface is shown in Fig. 9. Titanium oxide, TiO_2 , passive film, which is most usually found on the Ti surface, is not formed on the corroded surface. Instead of the Ti oxide, two types of titanium hydrides ($\text{TiH}_{1.924}$ and $\text{TiH}_{1.971}$) are unexpectedly found from the surface.

Titanium hydride is brittle and does not have corrosion resistant passive film properties which Ti oxide has. There-

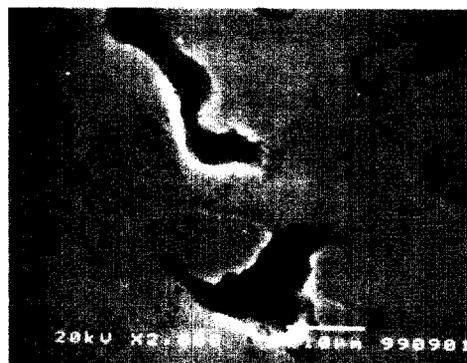


Fig. 6. SEM image of micro pore found at inner area.

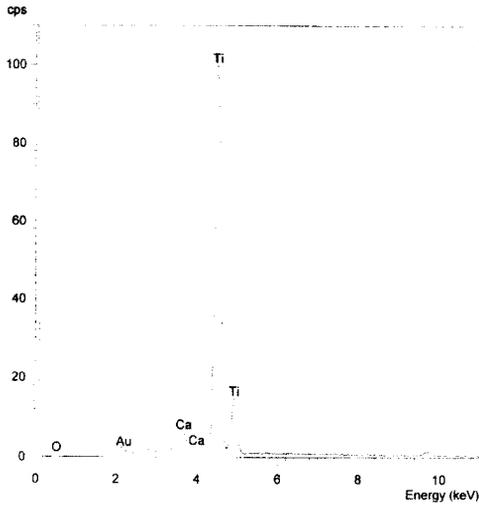
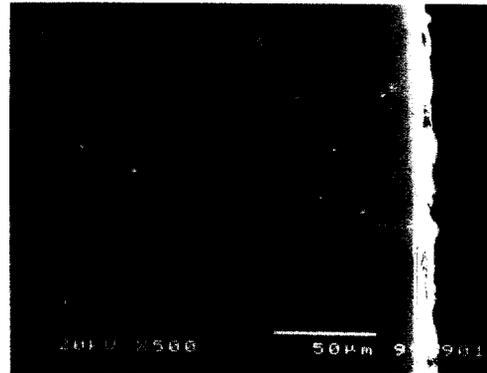


Fig. 7. EDX analysis result of the dark spot within the micro pore shown in Fig. 6.

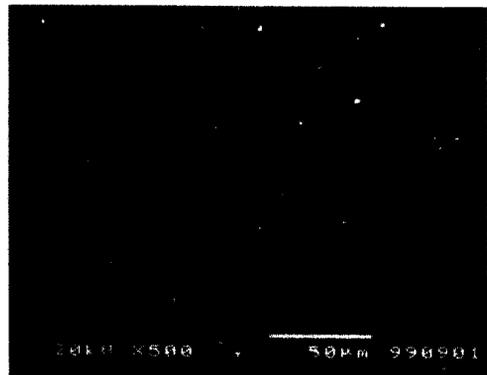
fore, when titanium hydride is formed on the surface, the corroded surface shows brittle behavior and is easily spalling off into small pieces.⁷⁾ The reason of Ti hydride formation and the corrosion mechanism of Ti are discussed in the next section.

2.4 Mechanism of Ti corrosion

The electrochemical reactions occurring at the electrodes are as the following.



(a)



(b)

Fig. 8. SEM images of a cross cut surface of the uncorroded fastener specimen. (a) near surface region, (b) inner area

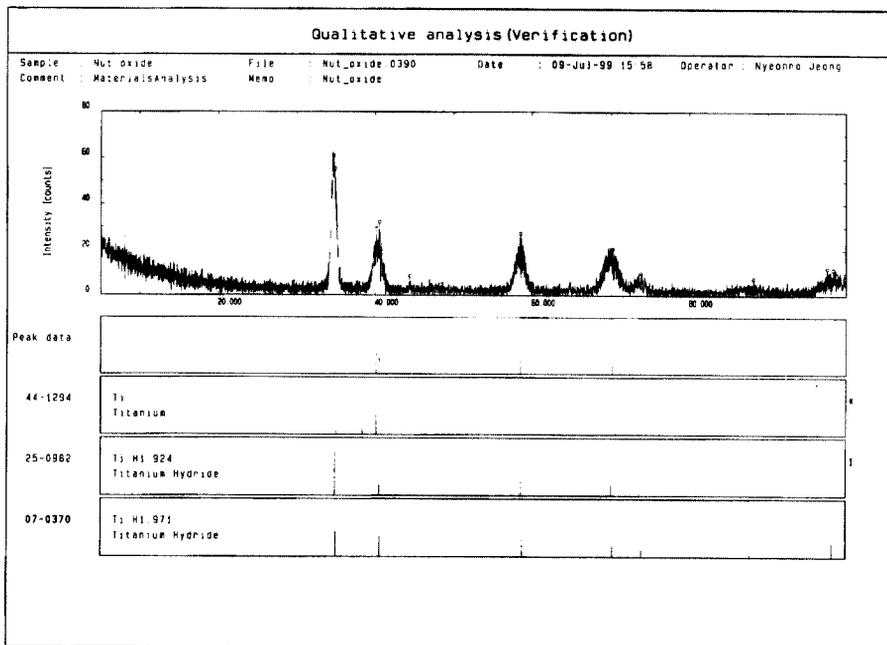
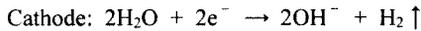
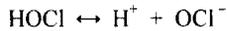
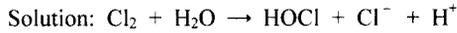


Fig. 9. XRD analysis of the corroded surface. Not the Titanium oxides, but the Titanium hydrides are found.



The evolved Cl_2 at anode is transformed into sodium hypochlorite (NaOCl) through the following reactions in the solution.¹⁾



Therefore, the reason of Ti hydride formation is believed due to the hydrogen evolved at the cathodes during the electro-chlorination process of sea water.

According to a research,⁸⁾ the critical hydrogen concentration, which can form titanium hydride on titanium, is about 150 ppm. However, this critical hydrogen concentration can be varied depending on many factors such as material purity, microstructure, and solution temperature etc. Therefore, the titanium hydride can be formed at as low as 40-50 ppm hydrogen concentration.^{8),9)}

Hydrogen concentration in a cell during the normal operation condition of the sea water electro-chlorination equipment could not be measured. However, it is calculated as about 70 ppm at maximum using the operation conditions of electrical voltage/current and flow rate etc. Therefore, the hydrogen concentration is believed to be high enough to form the titanium hydride, especially when the titanium has defects in it. That is, the titanium hydride formation is much more enhanced by the micro pores in the titanium, because of the easy diffusion of hydrogen into the material and the hydrogen partial pressure build up in the micro pores. Meanwhile, no titanium hydride layer was found from the surfaces of the uncorroded fasteners and spacers.

Since the titanium hydride can be developed only at the cathodes, due to the hydrogen evolution at cathodes, this is the reason why the fasteners and spacers for the cathodes only, not for the anodes, are corroded. Even in a corroded fastener or spacer, most of the degradation occurred at the area that is faced toward the anodes. This also results from that the electrolysis current is spatially not uniformly distributed, and therefore hydrogen evolution is more vigorous at the anode facing area.

3. Remedial measures

As the titanium fasteners spacers are corroded due to the Titanium hydride formation which was enhanced by the microstructural defects, following remedial measures are suggested.

1) The titanium fasteners and spacers that have micro pores in them should be replaced with the one which has not. This means that the wrought product should be used instead of power metallurgy products that have microstructural defects.

2) Installation of hydrogen separator into the sea water electro-chlorination equipment, which can decrease the hydrogen concentration in the cell solution, can reduce or retard the corrosion. However, this can not be a permanent solution as far as there are microstructural defects.

3) As the hydrogen evolution rate is increased with the operation current of the equipment, care should be given to the maximum operation current, which sometimes exceed the normal operation range to increase the biocide concentration.

4. Conclusions

Following conclusion are drawn from the titanium fasteners and spacers failure analysis results.

1) The unusual severe corrosion of titanium fasteners and spacers at cathode is due to the titanium hydride formation instead of titanium oxide at the surface.

2) The titanium hydride layer development was enhanced by the microstructural defects of micro pores, which is believed resulted from the improper powder metallurgy process.

3) The critical concentration of hydrogen for the formation of titanium hydride can be lowered significantly with the microstructural defects in titanium.

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